Direct resonance interaction with a cationic center

Direct resonance interaction with an anionic center

The underlying physical basis for the failure of Hammett σ_m and σ_p values to correlate certain reaction series is that all substituent interactions are some mixture of resonance and field effects. When direct resonance interaction is possible, the extent of the resonance increases and the substituent constants appropriate to a more "normal" mix of resonance and field effects then fail. There have been many attempts to develop sets of σ values that take into account extra resonance interactions.

One approach is to correct for the added resonance interaction. This is done in a modification of the Hammett equation known as the Yukawa–Tsuno equation[18]:

$$\log \frac{K}{K_0} = \rho\sigma + \rho(r)(\sigma^+ - \sigma) \tag{4.17}$$

The additional parameter r is adjusted from reaction to reaction; it reflects the extent of the additional resonance contribution. A large r corresponds to a reaction with a large resonance component, whereas when r goes to zero, the equation is identical to the original Hammett equation. When there is direct conjugation with an electron-rich reaction center, an equation analogous to Eq. (4.17) can be employed, but σ^- is used instead of σ^+.

The Yukawa–Tsuno relationship expanded to include both the σ^+ and σ^- constants is called the LArSR equation[19]:

$$\log \frac{k}{k_0} = \rho(\sigma^0 + r^+\Delta\sigma_R^+ + r^-\Delta\sigma_R^-)$$

In this equation, the substituent parameters $\Delta\sigma_R^+$ and $\Delta\sigma_R^-$ reflect the incremental resonance interaction with electron-demanding and electron-releasing reaction centers, respectively. The variables r^+ and r^- are established for a reaction series by regression analysis and are measures of the extent of the extra resonance contribution: the larger their value, the greater the extra resonance contribution. Since both donor and acceptor capacity will not contribute in a single reaction process, either r^+ or r^- would be expected to be zero.

18. Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.* **32**, 971 (1959); J. Hine, *J. Am. Chem. Soc.* **82**, 4877 (1960); B. M. Wepster, *J. Am. Chem. Soc.* **95**, 102 (1973).
19. Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.* **39**, 2274 (1966); Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.* **45**, 1210 (1972).